Integration of an Emerging Highly Sensitive Optical CO_2 Sensor for Ocean Monitoring on an Existing Data Acquisition System SeaKeeper 1000™ Annual Report for FY12 (Oct 1, 2011 – Sep 30, 2012)

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LONG-TERM GOALS

Develop a high-performance pCO_2 sensor that is affordable enough to be deployed in geat numbers to autonomously monitor the overall patterns of CO_2 emissions and ocean acidification.

OBJECTIVES

- Meet the challenging requirements for ocean pCO_2 monitoring using an innovative sensor design based on high sensitivity fluorescence detection.
- Assemble the system with low-cost optics and electronics in order to make it affordable enough (target cost <$1,000) to be deployed in greater numbers.
- Make the entire system drift and calibration free by perfecting a patch renewal process using an innovative microfluidics-based approach.
- Integrate the system into an existing platform system, the Seakeeper 1000™, to leverage already proven deployment systems readily amenable to autonomous operation.
- Test the reliability and robustness of the prototype system in the lab and open waters with our partners NOAA and Seakeepers International.
- Commercialize sensors with our industrial partner Fluorometrix Corporation.

APPROACH AND WORK PLAN

- Scientific and/or technical approach

The novelly designed optical sensor for autonomous ocean monitoring works on equilibrium principles. When the pH-sensitive reagent solution sitting behind a gas-permeable membrane is exposed to seawater, the CO_2 molecules present in the seawater diffuse across the membrane into the reagent and induce a pH change. After equilibrium is reached, the fluorescence is measured and the pCO_2 data are recovered from a calibration curve. A specific feature of our measurement technique is the use of excitation ratiometric approach. A violet LED (Light Emitting Diode) and a blue LED are used to excite the sensing reagent through an excitation filter and the pCO_2 dependent emission is measured through an emission filter by a photodiode. This approach is especially valuable from stability point of view – the chemical part that the sensor is based on is

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practically insensitive to the changes in temperature. Besides the ratiometric feature, the system also has a lot of other novel features including the ideal 90° separation between excitation and emission, the mirrored cavity, the beam combiner, and the renewal of the sensing reagent, etc. To greatly improve the sensitivity of the sensor, we ideally separated the excitation and the emission, leading to significantly reduced scattered light reaching the detector, thereby increasing the signal to noise ratio. The sensing reagent was placed in a mirrored cavity, allowing the excitation light to uniformly excite the dye. To address the photobleaching of the sensing reagent, we used a technique that automatically renews the sensing reagent after every measurement. This makes the measurements totally calibration-free.

- The key individuals participating in this work

Govind Rao, Ph.D., Professor, overall project management.
Yordan Kostov, Ph.D., Research Professor, electronics and optics design.
Xudong Ge, Ph.D., Research Associate Professor, reagent formulation and microfluidics design.
Robert Henderson, Graduate Student, system preparation and test etc.
Nick Selock, Graduate Student, system preparation and test etc.

- Work plans for the upcoming year

We will continue to optimize the system until the long-term goal is realized.

WORK COMPLETED

- Designed and built the excitation and read out system with low-cost optics and electronics.
- Designed and built the microfluidic system including the equilibrium chamber and the measurement chamber.
- Optimized the sensing patch formulation, found the best dye or dye combinations to meet the requirements for measuring ranges, found the optimal dye and base concentrations to satisfy the required sensitivity, and found the best semipermeable material for pCO_2 sensing.
- Prototype systems were presented and examined at NOAA’s AOML location.

RESULTS

- The new flow cell

The previous flow cell was made of PMMA, which has been replaced with glass. The PMMA was found to fluoresce and absorb the signal fluorescence to a significant degree, which likely contributed to noise. The material previously used was simple enough to put together in a bonded fluidics chip, but using glass requires cutting small pipettes and using graphite ferrules at the ends. The flow cell currently requires PEEK fittings to be screwed into PEEK bulkheads using the graphite ferrules (as opposed to impermeable PEEK ferrules) so that the glass itself doesn’t crack upon tightening.

- The best pump system

The pump used for the pCO_2 sensor had been a 12-gear peristaltic pump currently out of production. It used 1/8” OD impermeable rubber tubing and was approximately 150 cubic inches. As it was out of production, another pump had to be found. Several pumps were evaluated for usage including the Lee Co LPLA1210550L, the Bartels MP6, the BASi Bee, the Cole Palmer 7553-20 and the Dolomite 3200243. In addition to the above pumps, several alternative measures for non-contact pumping have also been explored. The simple design used a normally-closed valve, which contained fluid from the pressurized dye bag. Pressure was applied from a large mass on top of the chamber. This was abandoned when the issues with the dye bag could not be overcome. The more complex design involved pressurizing a N_2 sparged container, rather than the dye bag. Finally, the Dolomite pump within a N_2 sparged chamber was selected as the best pump system.

- The new mass exchanger

Although the previous mass exchanger had the benefits of being impermeable to CO_2 exchange from the outside and showed mixed plug flow properties from a residence time distribution, it did not meet the size specifications required for deployment. To this end, a concentric tube mass exchanger shown in Figure 1 has been developed. The same Teflon 2400 capillary tubing (0.032” OD and 0.024” ID) was used as our exchange membrane tubing (again due to its exceptional gas permeability), with Tygon gas proof tubing on the outside. The length of the membrane has been cut in order to accommodate the slightly slower Dolomite pump used.

Figure 1. The concentric tube mass exchanger. The yellow is the Tygon tubing. The blue inside the Tygon tubing is the sea water. The green is the Teflon tubing with the HPTS dye solution inside.

- The baseline testing

The objective of the baseline testing was to see if (1) the flow system had any small dead volumes which might hold dye with at a different pH and (2) if there is a chance that there is back-diffusion of the hydrogen ions down the line itself. Testing involved running buffered HPTS, pure water and APTS through the system. The tests showed the dead volumes did exist, hence a new flow system was designed as described above. To counter-act the back diffusion of

the hydrogen ions, a normally closed valve has been put in place between the mass exchanger and the optics chamber. This has a secondary benefit of minimizing the light allowed down the line.

Alternative arrangements for the timing cycles shown in Figure 2 have been considered. Below 400 warm up cycles, the reference values drift significantly, so 500 has been chosen to act as a safe number. Baseline readings have also been attempted with LEDs left on, which did not improve LED stability, and for alternative time periods between testing. Tests two hours apart seem to have more steady reference LED intensities within trials (no drift during the reading) but still showed change over time. Although it would be preferable to steady this, the fluorescent intensities are normalized with respect to the LED intensity, so the long term change should not be a large issue and the short term solution seems to be spacing tests two hours apart.

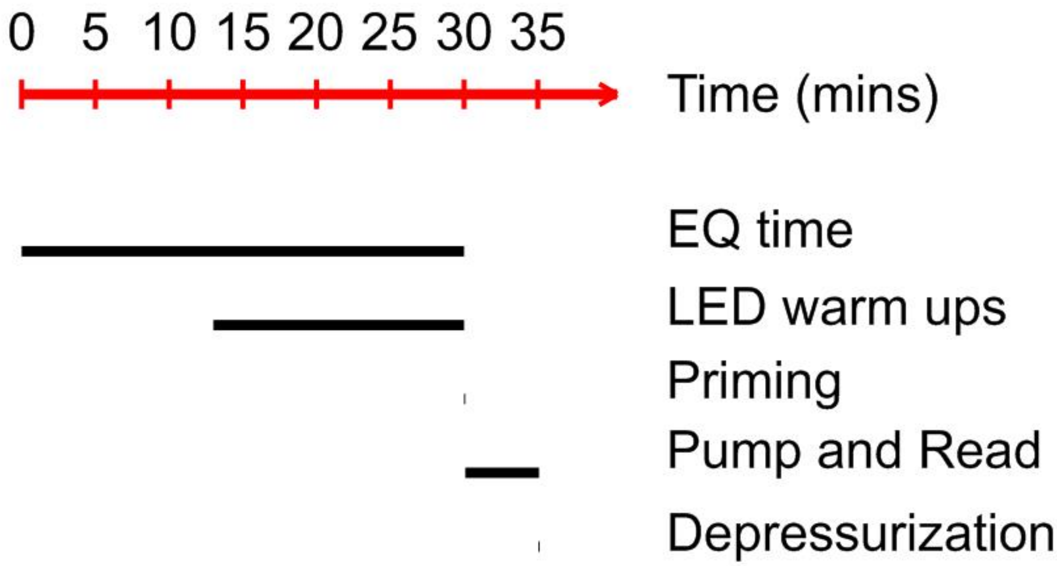

Figure 2. The timing cycles of the sensor system. The LED warm-up cycle involves flashing both LEDs 500 times.

- Calibration

A sparged gas system with the new mass exchanger, pump, plumbing and timing cycles has been built and is currently being investigated. Several calibration curves have been made using the dye bag system.

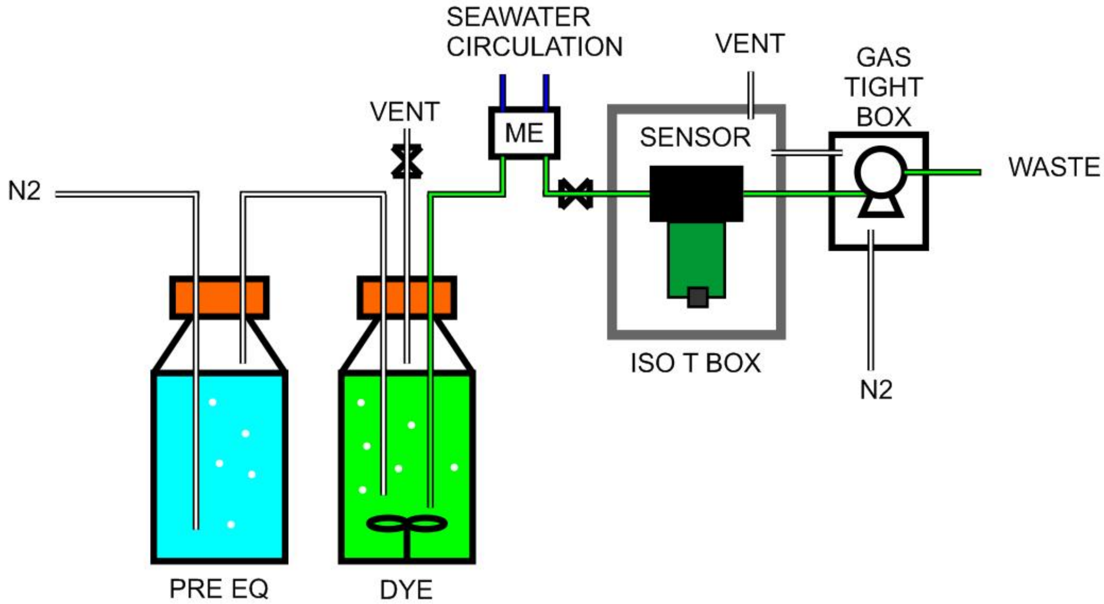

Figure 3. The latest sensor set up. Nitrogen gas is humidified in the PRE-EQ chamber, before being sparged into the dye reservoir (DYE) chamber. The dye is agitated and pulled through a the mass exchanger (ME), where it is allowed to exchange CO_2 with the seawater. It is then pulled through the optoelectronics of the sensor within a container with temperature control, which is held under a nitrogen blanket- the same one used to keep CO_2 out of the Dolomite pump used to pull the dye through the system.

IMPACT AND APPLICATIONS

National Security

Global warming caused by increasing amount of CO_2 discharged into the environment by human activity is usually characterized as an environmental threat, but now it has been realized that it is also an issue of national security. Unchecked global warming could raise the sea levels, change the amount and pattern of precipitation, and increase the intensity of extreme weather events and change the agricultural yields, leading to large-scale migrations, increased border tensions, the spread of disease and conflicts over food and water. All could lead to direct involvement by the United States military. The pCO_2 sensor being developed will surely have a great impact on the war against global warming. As the sensor being developed will be highly sensitive, and highly stable, yet affordable enough to be deployed in great numbers, the overall pattern of greenhouse gas emissions in an area can be monitored autonomously. Accurately and precisely measuring is the first critical step to control global warning and to alleviate the severity of its effects.

Economic Development

The economic sector most affected by global warming will be the agricultural sector because global warming will seriously affect the number of rainfall. In some regions, the overall frequency of droughts will become longer and more intense. While in other areas, there will be too much rainfall, leading to flooding. Another globally important economic activity most

affected by global warming will be fisheries. Due to their primitive nature, the output of fisheries is directly and strongly affected by variations in natural conditions. The pCO_2 sensor being developed will monitor the pCO_2 levels and help alleviate the harmful effects.

Quality of Life

Fisheries are closely tied to human health and species health across the globe. Widespread changes in quality of life will occur if global warming continues at its current pace. More frequent heat waves and a significant increase in days with poor air quality could endanger the elderly and children.

TRANSITIONS

Economic Development

Discussions are underway with a major manufacturer of environmental sensors to fast-track deployment of the pCO_2 sensors.

RELATED PROJECTS

None

PUBLICATIONS

Xudong Ge, Yordan Kostov, Robert Henderson, Nick Selock, Govind Rao. A low-cost high-performance fluorescence detector for measurements of pCO_2 in seawater (submitted).

Xudong Ge, Robert Henderson, Yordan Kostov, Govind Rao. Low-cost fluorescence-based microfluidic sensor for measurements of pCO_2 in seawater. Ocean Sensing and Monitoring IV, April 23-27, 2012, Baltimore, MD, USA.

Yordan Kostov, Xudong Ge, Robert Henderson, Govind Rao. Fluorescence-based microfluidic sensor for measurements of pCO_2 in seawater. PITTCON Conference & Expo 2012, March 11-15, 2012, Orlando, FL, USA.

PATENTS

A new US Patent Provisional Application was filed this year. The application is entitled “Analyte Sensing System and Method Utilizing Separate Equilibrium and Measurement Chambers” and the Application Serial No. is 51/388,219.